Long-Term Effects of Dredging Operations Program

Leachate Testing and Evaluation for Freshwater Sediments

by James M. Brannon, Tommy E. Myers, Barbara A. Tardy

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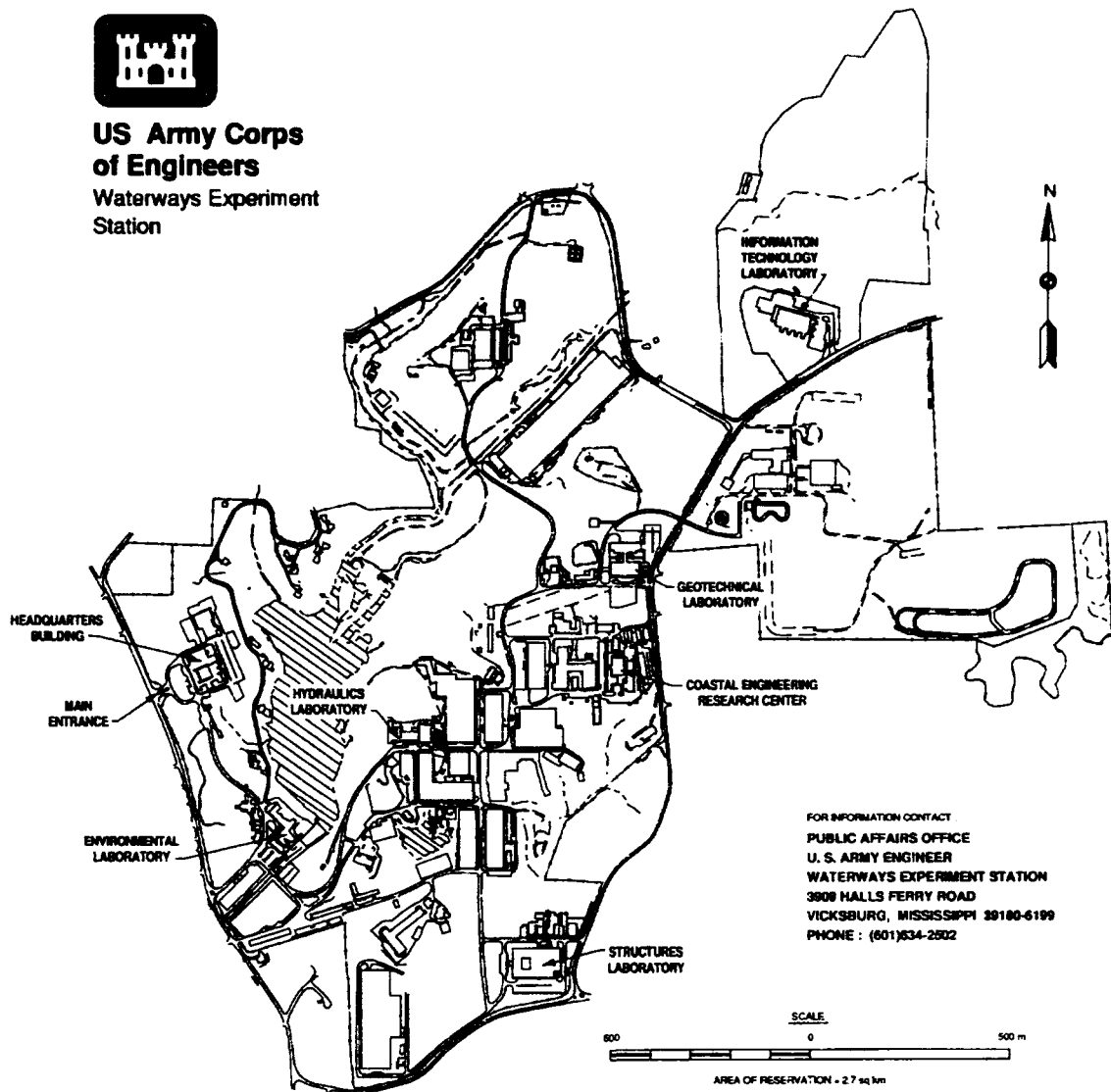Vicksburg, MS 39180-6199

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SCALE
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Contents

Preface

This report was prepared by Dr. James M. Brannon, Ecosystem Processes and Effects Branch (EPEB), Environmental Processes and Effects Division (EPED), Environmental Laboratory (EL), and Mr. Tommy E. Myers and Ms. Barbara A. Tardy, Environmental Restoration Branch (ERB), Environmental Engineering Division (EED), EL. Dr. Judith C. Pennington, EPEB, and Dr. Donald Dean Adrian, Louisiana State University, Baton Rouge, LA, were technical reviewers for this report. Funds for this work were provided by the Long-Term Effects of Dredging Operations (LEDO) Program. LEDO is managed within the Office of Environmental Effects of Dredging Programs (EEDP) at WES. Dr. Robert M. Engler is Manager of EEDP. The HQUSACE Technical Monitors for LEDO were Mr. Dave Mathis and Mr. Joe Wilson.

The work was conducted under the direct supervision of Dr. Richard E. Price, Acting Chief, EPEB, Mr. Norman R. Francingues, Jr., Chief, ERB, and under the general supervision of Mr. Donald L. Robey, Chief, EPED, Dr. Raymond L. Montgomery, Chief, EED, and Dr. John Harrison, Director, EL.

During publication of this report, Dr. Robert W. Whalin was Director of WES. COL Bruce K. Howard, EN, was Commander.

This report should be cited as follows:

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Conversion Factors, Non-SI to SI Units of Measurement

Non-SI units of measurement used in this report can be converted to SI units as follows:

Multiply	By	To Obtain
gallons (U.S. liquid)	3.785412	cubic decimeters
inches	0.0254	meters

1 Introduction

Background

Contaminated dredged material is often placed in confined disposal facilities (CDFs) designed and operated to control environmental impacts of the disposed material. A CDF is a diked enclosure having either permeable or low-permeable walls that are used to retain dredged material solids. CDFs can either be completely upland or nearshore (either partially or totally surrounded by water). When contaminated dredged material is placed in a CDF, contaminants may be mobilized to form leachate which is transported to the site boundaries by seepage. A general CDF configuration and potential contaminant leachate loss pathways are shown in Figure 1. Subsurface drainage and seepage through dikes may reach adjacent surface and ground waters and act as a source of contamination. Since the contaminants present in dredged material are adsorbed to sediment particles, leaching by percolating site water for a CDF situated above the groundwater table is the primary mechanism by which contaminant migration to groundwater takes place. If the site is situated so that groundwater will flow through the material, percolating groundwater may be the primary source of water through the material.

Figure 1. Contaminant migration pathway: leachate seepage

Leachate from dredged material placed in a disposal site is produced by three potential sources: the original pore water, rainfall infiltration, and, especially for nearshore sites, groundwater or surface water in contact with the dredged material as a result of fluctuating water levels.

Leachate generation and transport in a CDF depend on site-specific hydrology, engineering controls at the disposal site, dredged material hydraulic conductivity, initial water content, and nature of contaminants. Immediately after dredging and disposal, dredged material is saturated (all voids are filled with water). As evaporation and seepage remove water from the voids, the amount of water stored and available for gravity drainage decreases. To predict time-varying leachate flow, all these factors must be considered. Therefore, generation of leachate test data must be combined with tools for predicting mass flow of water through a CDF in order to conduct site-specific evaluations.

Objective

The objective of this report is to provide recommended procedures for conducting batch and column leachate evaluations for freshwater sediments. Guidance for use of results in site-specific leachate evaluations is also provided.

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2 Theoretical Basis for Leachate Quality Evaluations

This chapter briefly summarizes the theoretical basis for leachate quality evaluations used to develop the recommended test procedures. Detailed explanations of leachate theory can be found in Hill, Myers, and Brannon (1988), Myers and Brannon (1988a), and Myers, Brannon, and Price (1992).

Nature of the Problem

Contaminant migration via leachate seepage is a porous-medium contaminant transport problem (Figure 2). Leaching is defined as interphase transfer of contaminants from dredged material solids to the pore water surrounding the solids and the subsequent transport of these contaminants by pore water seepage. Thus, leaching is interphase mass transfer (Equation 2 in Figure 2) coupled with porous-media fluid mechanics (Equation 1 in Figure 2). Interphase mass transfer during dredged material leaching is a complicated interaction of many elementary processes and factors affecting these processes (Figure 3). A complete description of all these processes, of their interactions, and of factors affecting these processes is not presently possible. Instead, a lumped parameter, the distribution coefficient, is used to describe the distribution of contaminant between aqueous and solid phases.

Equilibrium Assumption

In order for contaminants to cross the interface between dredged material solids and water, a difference in chemical potentials must exist. Chemicals flow from a region of high chemical potential to a region of low chemical potential just as electric current flows from a region of high

MASS FLUX IN

ΔY

ΔX

Z

ΔZ

Z·ΔZ

MASS FLUX OUT

DM

$$D_p \frac{\partial^2 C_i}{\partial z^2} - V \frac{\partial C_i}{\partial z} + S = \frac{\partial C_i}{\partial t}$$ (1)

$$S = \frac{\rho_b}{n} \frac{\partial q_i}{\partial t}$$ (2)

where

D_p = dispersion coefficient for ith contaminant, m^2/sec

C_i = pore water concentration of ith contaminant, mg/L

z = space dimension, m

V = average pore water velocity, m/sec

S = interphase contaminant transfer, mg/L sec

t = time, sec

ρ_b = bulk density, kg/L

n = porosity, dimensionless

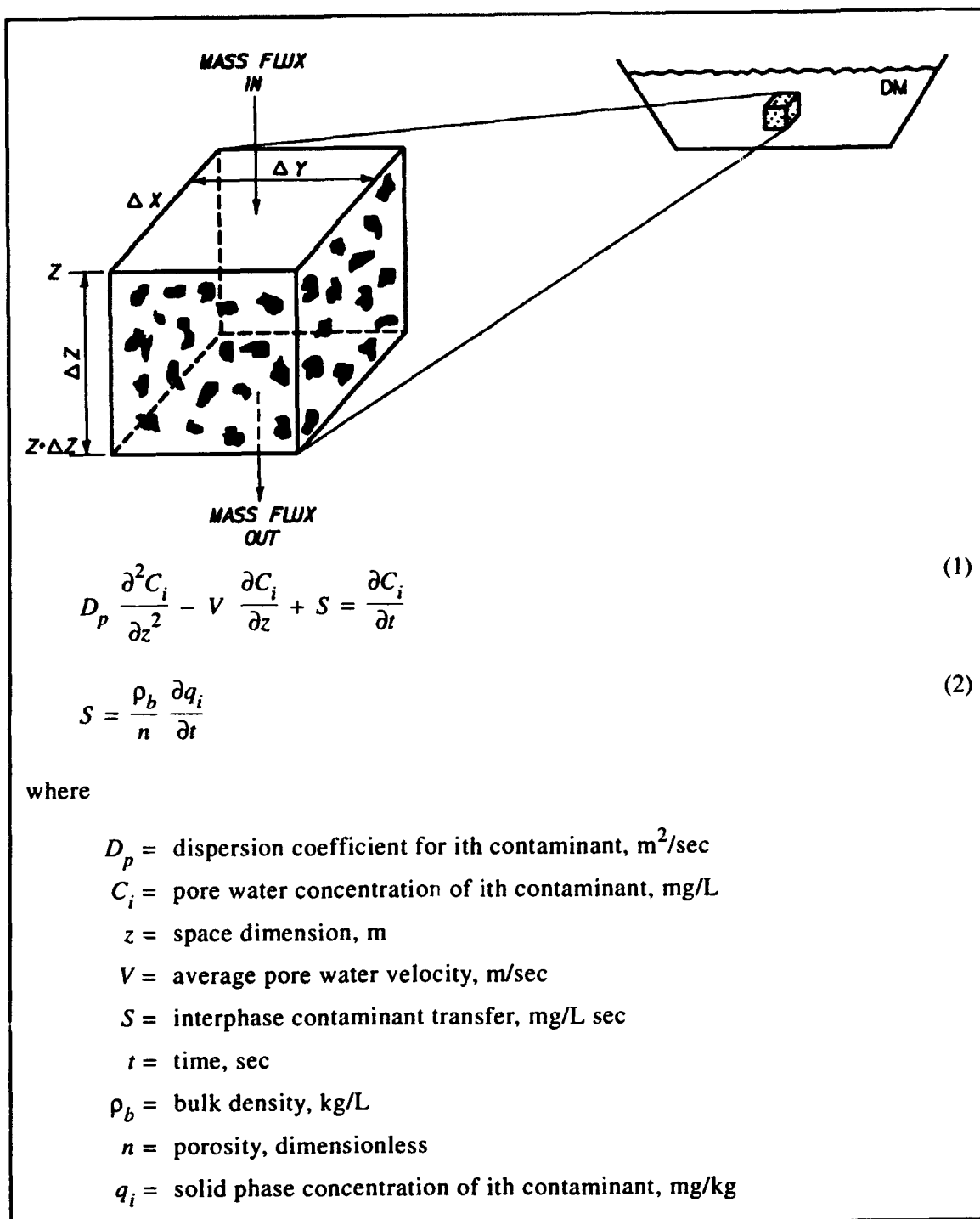q_i = solid phase concentration of ith contaminant, mg/kg

Figure 2.   Mathematical model of dredged material leaching (Hill, Myers, and Brannon 1988)
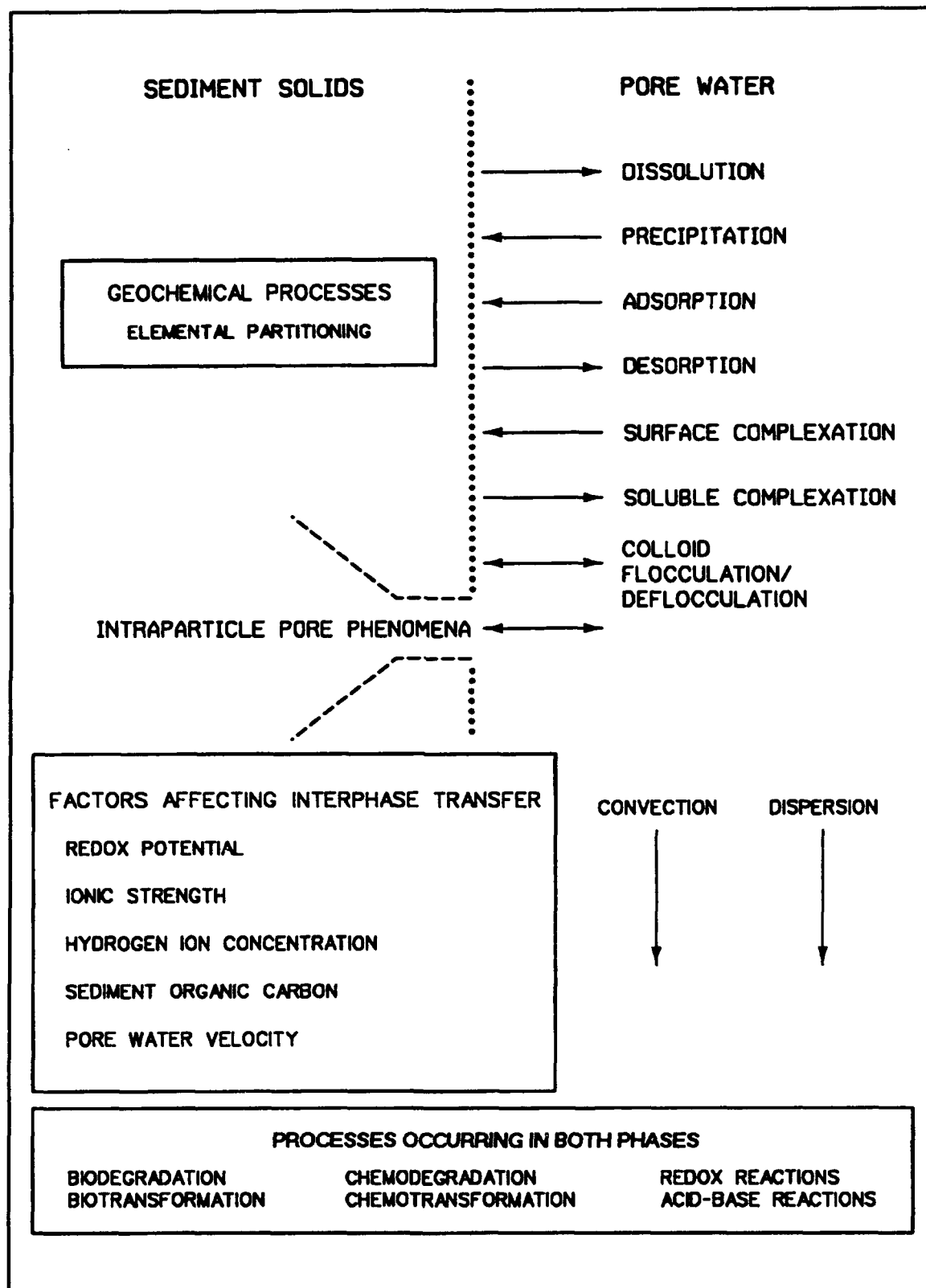
Figure 3. Interphase transfer processes and factors affecting interphase transfer processes

electrical potential to one of lower electrical potential, or as mass flows from a position of high gravitational potential to one of low gravitational potential. When chemical potentials are equal, the net transfer of contaminant across the solid-water interface is zero, and the mass of contaminant in each phase is constant, but not necessarily equal. The processes shown in Figure 3 control the rate at which equilibrium is reached and the equilibrium distribution of contaminant between solid and aqueous phases. Once equilibrium is reached, the ratio of contaminant mass in the solid phase to the contaminant mass in the aqueous phases does not change.

In practice, a true equilibrium between dredged material solids and pore water never exists because some of the processes shown in Figure 3 have very slow reaction rates. However, steady-state can be reached between dredged material solids and water if an operational definition of equilibrium is used. In this report, equilibrium is operationally defined for the batch leach tests as the condition at which changes in leachate contaminant concentrations with time cannot be measured; that is, differences are not statistically significant.

By assuming equilibrium between solid and aqueous phases, the need for determining controlling processes and the rate coefficients for these processes is eliminated. Without the equilibrium assumption, laboratory testing and mathematical modeling would require determination of controlling processes and investigation of the kinetics for these processes. As is apparent from Figure 3, predictive laboratory tests and mathematical models based on chemical and mass transfer kinetics would be too complicated for routine application to dredged material leaching. Thus, application of the equilibrium assumption is imperative for the development of predictive techniques suitable for routine use.

Once equilibrium has been reached, only the relative distribution of contaminant between solid and aqueous phases is needed to predict leachate quality. This distribution is conveniently represented by the equilibrium distribution coefficient defined as follows:

$$K_d = \frac{\dfrac{M_{cs}}{M_s}}{\dfrac{M_{cw}}{M_w}} \qquad (3)$$

where

K_d = equilibrium distribution coefficient, dimensionless

M_{cs} = mass of contaminant in the solid phase, kg

M_s = mass of solids, kg

M_{cw} = mass of contaminant in the aqueous phase, kg

M_w = mass of water, kg

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The mass fractions in Equation 3 can be replaced with phase contaminant concentrations without any loss of generality so that Equation 3 becomes:

$$K_d = \frac{q}{C} \qquad (4)$$

where

K_d = equilibrium distribution coefficient, L/kg

q = contaminant concentration in the solid phase at equilibrium, mg/kg

C = contaminant concentration in the aqueous phase at equilibrium, mg/L

Equations 3 and 4 describe the equilibrium distribution of a single contaminant in a dredged material; that is, equilibrium distribution coefficients are contaminant and dredged material specific. As will be discussed in a later section, K_d is affected by various factors (sediment oxidation status, time of contact, liquid to solid ratio, pH, and ionic strength). Varying these factors during leaching can shift the equilibrium position of the system and change K_d.

Equilibrium-Controlled Desorption in a CDF

The assumption of equilibrium-controlled desorption in a CDF is based on two arguments: (a) the intuitive argument that the interphase transfer rates affecting leachate quality are fast relative to the volumetric flux of water in the CDF, and (b) the argument that equilibrium-controlled desorption provides conservative predictions of leachate quality. This section discusses these arguments. The term "desorption" as used here and in the remainder of the report refers to the composite effect of the elementary interphase transfer processes shown in Figure 3.

Contaminated dredged materials are usually fine-grained and have hydraulic conductivities in the range of 10^{-5} to 10^{-8} cm/sec. When the hydraulic conductivity is this low, pore water velocities are also low. In filled CDFs, the hydraulic gradient is rarely larger than one, so that pore water velocities approximate hydraulic conductivities; that is, the water moves very slowly at velocities of 10^{-8} to 10^{-5} cm/sec.

When the rate at which water moves is slow relative to the rate at which equilibrium is approached, a local chemical equilibrium exists between the pore water and the sediment solids. The local equilibrium concept is illustrated in Figure 4. The local equilibrium assumption implies that as a parcel of water passes a parcel of dredged material solids, the water and solids come to chemical equilibrium before the parcel of water

Figure 4.   Illustration of the local equilibrium assumption for leaching in a CDF

moves to contact the next parcel of dredged material solids. Leachate quality at the surface of a CDF will differ from leachate quality at the bottom of a CDF, while leachate in both locations will be in equilibrium with the dredged material solids. Some soil column studies have indicated that the local equilibrium assumption is valid for pore water velocities as high as 10^{-5} cm/sec (Valocchi 1985). In reality, equilibrium-controlled desorption requires an infinitely fast desorption rate. However, if the critical interphase transfer rates are sufficiently fast, the equilibrium assumption can yield results indistinguishable from full kinetic modeling (Jennings and Kirkner 1984; Valocchi 1985; Bahr and Rubin 1987).

In addition to being a good approximation, the assumption of equilibrium-controlled desorption is conservative; that is, predictions based on the equilibrium assumption will overestimate leachate contaminant concentrations for dredged material. The equilibrium assumption is conservative because interphase transfer is from the dredged material

solids to the pore water, and equilibrium means that all of the desorption that can occur has occurred. Thus, for clean water entering the dredged material, pore water contaminant concentrations cannot be higher than the equilibrium value.

3 Sequential Batch Leach Tests

Background

Batch leaching is a procedure for determining how contaminant mass is distributed between solid q and aqueous phases C at equilibrium. Sequential batch leaching is a procedure for determining how the equilibrium distribution of contaminant between solid phase and aqueous phase changes during elution with water. Details are described in the section on recommended procedures. A relationship between q and C is needed to evaluate the source term S in the mathematical model shown in Figure 2. The source term is obtained by using the chain rule as follows:

$$S = -\frac{\rho_b}{n}\frac{\partial q}{\partial t} = -\frac{\rho_b}{n}\frac{\partial q}{\partial C}\frac{\partial C}{\partial t} \tag{5}$$

The term $\partial q/\partial C$ represents the functional dependence of leachate quality on contaminant levels in the dredged material solids. The sequential batch leach tests (SBLT) provide the information needed to evaluate $\partial q/\partial C$.

By sequentially leaching an aliquot of sediment solids, a table of solid phase contaminant concentrations q and aqueous phase contaminant concentrations C can be developed and plotted (successive batches have differing q and C concentrations). A plot of q versus C yields a desorption isotherm, the slope of which is the distribution coefficient. Several types of desorption isotherms have been observed in SBLTs for sediments (Environmental Laboratory 1987; Myers and Brannon 1988b; Palermo et al. 1989; Brannon, Myers, and Price 1990; Myers, Brannon, and Price 1992). The two most important types are discussed below.

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Constant K_d

Sequential batch leaching of freshwater sediments usually yields desorption isotherms such as shown in Figure 5. This is referred to as a classical desorption isotherm. Its key feature is a single distribution coefficient that is constant throughout the sequential leaching procedure. A commonly observed feature of desorption isotherms for metals in freshwater sediments is that they do not go through the origin, but intercept the ordinate at some other point. The intercept indicates the amount of metal in geochemical phases that is resistant to aqueous leaching.

The general form of the q versus C relationship for classical desorption isotherms is as follows:
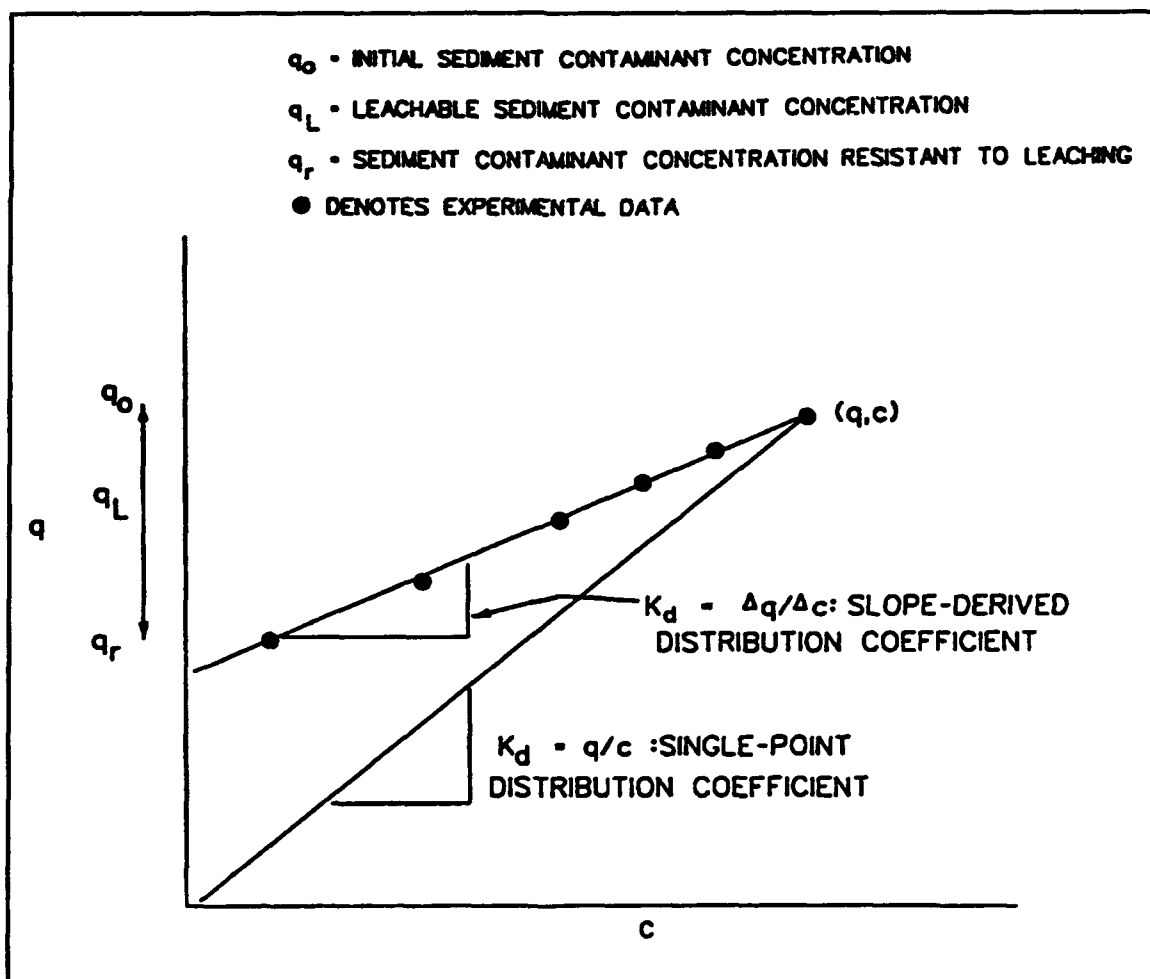
$$q = K_d C + q_r \tag{6}$$

Figure 5.   Desorption isotherms for slope-derived and single-point distribution coefficients

where q_r = solid phase concentration resistant to leaching, mg/kg. Differentiating Equation 6 with respect to time yields

$$\frac{\partial q}{\partial C} = K_d \tag{7}$$

The source term S in Equation 1 is obtained by substituting K_d for $\partial q/\partial C$ in Equation 5.

Nonconstant K_d

Nonconstant distribution of contaminants between dredged material solids and water is not commonly observed during leaching of freshwater sediments. Isotherms with nonconstant K_d are primarily observed during leaching of estuarine sediments (Brannon et al. 1989; Brannon, Myers, and Price 1990; Brannon et al. 1991). Nonconstant contaminant partitioning yields an isotherm for which the distribution coefficient changes as the solid phase concentration q decreases during sequential leaching until a turning point is reached (Figure 6). At the turning point, the distribution coefficient becomes constant, and desorption begins to follow the classical isotherm. The nonconstant distribution coefficient portion of the desorption isotherm is related to elution of salt.

As salt is eluted from estuarine sediments, the ionic strength of the aqueous phase is reduced. According to the Gouy-Chapman model of charge distribution in double layers, decreasing the ionic strength increases repulsive forces (Stumm and Morgan 1981) so that flocculated colloidal matter becomes dispersed. Deflocculation of sediment organic carbon increases the concentration of dissolved organic carbon (DOC) in the aqueous phase, mobilizing metals and organic contaminants bound to the colloidal matter (Brannon et al. 1991). For these reasons, the type of desorption isotherm shown in Figure 6 is referred to as a DOC-facilitated desorption isotherm. Since the relationship of q versus C is not a one-to-one correspondence for DOC-facilitated desorption isotherms, q as a function of C cannot be developed from the isotherm. Research is continuing on how to model $\partial q/\partial C$ with K_d as a variable.

Recommended Procedure

The SBLT is recommended for use with freshwater sediments as a conservative estimate of leachate concentrations. Contaminant concentrations in the SBLT are usually higher than contaminant concentrations in column leach effluents (Environmental Laboratory 1987; Brannon, Myers, and Price 1992). Sequential batch leaching of freshwater sediments generally produces either a well-defined linear isotherm (Figure 7) or a clustered isotherm (Figure 8) (Myers and Brannon 1988; Brannon et al. 1989; Brannon, Myers, and Price 1990). Leaching of metals from anaerobic

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Figure 6. Desorption isotherm illustrating nonconstant and constant partitioning

freshwater sediment generally follows the expected pattern of metal re-
lease; that is, a sequence of decreasing metals concentrations is measured
during sequential batch leaching. This pattern generally occurs even if
the resulting isotherm is insufficiently regular to allow derivation of a
slope-derived K_d. Clustered isotherms result when aqueous phase contami-
nant concentrations are similar in all steps of the SBLT and are most com-
monly observed for organic contaminants.

Figure 7. Example of linear desorption isotherm from SBLT for zinc and cadmium in freshwater sediment

Figure 8. Example of clustered desorption isotherm from SBLT for polychlorinated biphenyls in freshwater sediment

The effects of liquid-solid ratio, kinetics, and oxidation status of the sediment during leaching have been discussed in detail in Myers and Brannon (1988b); Brannon et al. (1989); Brannon, Myers, and Price (1990); Myers and Brannon (1991); Myers, Brannon, and Price (1992); and Myers and Brannon (1993). Therefore, only a brief summary of the impacts of each of these factors and the reasons for choosing the recommended technique will be discussed.

Liquid-solid ratio

Batch testing has been conducted to find the optimum sediment-water ratio. Test results on nine sediments (Myers and Brannon 1993) indicated that a 4:1 ratio of water-to-sediment solids by weight is the highest ratio that can be used without solids concentration effects becoming important. The effects of sediment-to-water ratios do not follow well- defined trends and can bias leachate results in unpredictable directions (Brannon et al. in press). For this reason, a sediment-to-water concentration as close as possible to that which will exist in a CDF is important.

Time of contact

Contact time in a batch leach test, such as the SBLT, refers to the lapse time between introduction and removal of water. Experiments consistently demonstrate that a contact time of 24 hr is sufficient to achieve steady-state conditions for organics in leachate (Figure 9) (Environmental Laboratory 1987; Myers and Brannon 1988a; Myers and Brannon 1988b; Palermo et al. 1989; Brannon, Meyers, and Price 1990).

The kinetic behavior of metals is more complex than the behavior of organics (Brannon, Myers, and Price 1990). Metals generally show either no significant change in leachate concentrations over time or a peak in concentration following 1 day of contact. Either way, a contact time of 24 hr is appropriate.

Oxidation status of sediment

Development of the SBLT has also included batch testing of anaerobic and aerobic sediment. Leaching of aerobic, aged sediment has been used to simulate leaching of the surface crust in a CDF, and anaerobic leaching has been used to simulate leaching in the saturated-anaerobic zone of a CDF. Neither hydraulic nor mechanical dredging adds sufficient oxygen to overcome the sediment oxygen demand of polluted sediments. As a result, the dredged material in a CDF is anaerobic, except for a surface crust that develops as the CDF dewaters by evaporation and seepage. The oxidized crust may eventually be several feet thick, but, in general, never represents a significant portion of the vertical profile for the typically fine-grained material. The procedure below, therefore, describes the technique for anaerobic leaching. The technique for aerobic leaching is described in Environmental Laboratory (1987), Myers and Brannon (1988b), Palermo et al. (1989), and Brannon, Myers, and Price (1992). The aerobic leaching procedure may be necessary if the dredged material is to be applied in a thin layer as in, for example, land farming.

SBLT Test Procedure

The recommended procedure for anaerobic sequential batch leaching of sediments and dredged material is as follows:

a. *Step 1.* Load sediment into appropriate centrifuge tubes fitted with leakproof, airtight tops: 250 or 500 mL polycarbonate for metals and 450 mL stainless steel for organic contaminants. Add sufficient deoxygenated distilled-deionized water to each tube to bring final water-to-sediment ratio to 4:1. All operations should be conducted in a glove box under a nitrogen atmosphere.

Figure 9. Effect of time of contact on polyaromatic hydrocarbon leachate concentrations

b. *Step 2.* Place centrifuge tubes in a rotary tumbler such as described by Garrett et al. (1984) and turn at 40 rpm for 24 hr.

c. *Step 3.* Centrifuge for 30 min at 9,000 × g for metals and 6,500 × g for organics.

d. *Step 4.* Filter leachate through a 0.45-μm membrane filter for metals and a Whatman GD/F glass-fiber prefilter followed by a Gelman AE glass-fiber filter (1.0 μm nominal pore size) for organics.

e. *Step 5.* Set aside a small amount of leachate for analysis of pH and electrical conductivity. Acidify leachate with 1 mL of concentrated HCl or Ultrex nitric acid per liter of leachate for metals and organics, respectively. Store samples in the dark. Sample bottles should be cleaned to Environmental Protection Agency specifications or commercially purchased precleaned bottles should be used; polycarbonate for metals and glass for organics should be used. Bottles for organics should be filled to the top.

f. *Step 6.* Return to Step 2 after replacing leachate removed in Step 4 with fresh deoxygenated distilled-deionized water. Repeat the entire procedure to obtain a minimum of four complete sequential cycles.

Additional details are provided in Appendix A.

4 Column Leach Tests

Column leach tests, while not recommended for routine use, may be utilized if the contamination potential of the dredged material is very high and independent confirmation of batch test results is desired.

Background

Batch leaching tests, useful for determining desorption kinetics, equilibrium distribution coefficients, and long-term leaching characteristics, cannot simulate advective-dispersive and other mass transfer effects occurring in CDFs. Column leach tests are being used as laboratory-scale physical models of contaminant elution from dredged material that include advective-dispersive and other mass transfer effects. The primary purpose of column leaching is to demonstrate that the data from batch tests can be used to predict contaminant leaching in a CDF.

Recommended Method

A divided flow permeameter was used in many of the early leaching studies with dredged materials (Environmental Laboratory 1987, Myers and Brannon 1988a, Palermo et al. 1989). Problems with the apparatus, primarily the extended time needed to elute the number of pore volumes necessary for leachate evaluation and the potential for sample deterioration during collection (Myers and Brannon 1988b), prompted redesign of the column apparatus. The improved column design (Myers, Gambrell, and Tittlebaum 1991) is being used in current column leaching studies (Figure 10)[1] and is recommended for use where column studies are required. Appendices provide details of column assembly and loading (Appendix B), collection and preservation of leachate samples for inorganic constituents and total organic carbon (Appendix C) and organic

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[1] A table of factors for converting non-SI units of measurement to SI units is presented on page vi.
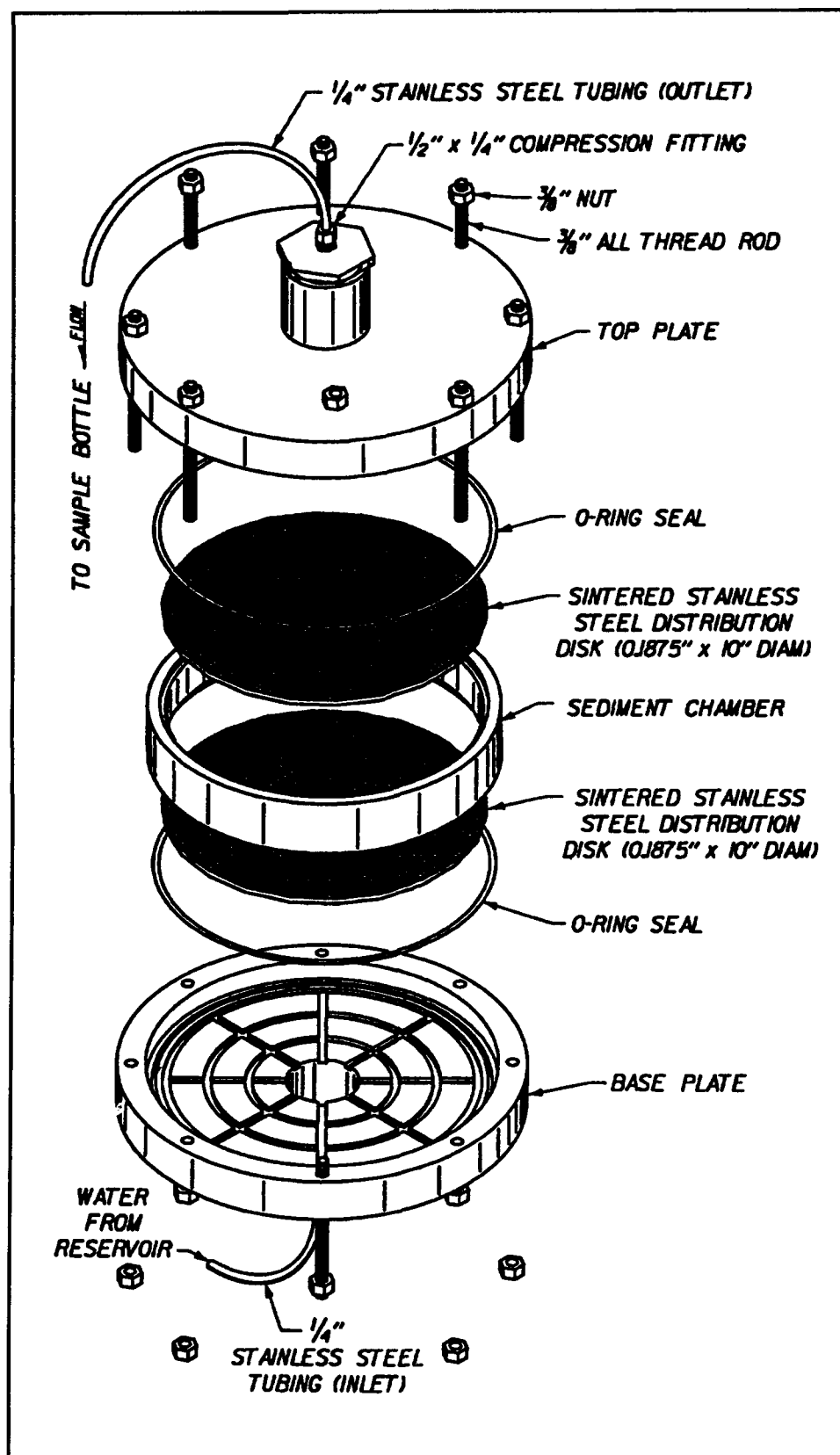
Figure 10. Thin-layer column

contaminants (Appendix D), analysis for total metals (Appendix E), and determination of chloride ion concentration (Appendix F) and bromide ion concentration (Appendix G). A brief description of the thin layer column is given in the following paragraphs.

To increase the number of pore volumes eluted in a given period of time, column length was reduced. Pore water velocity (flow) could have been increased, but pore water velocity affects the processes controlling contaminant release (Rubin 1983; Valocchi 1985; Bahr and Rubin 1987; Brusseau and Rao 1989). Therefore, adjustments must be made cautiously and judiciously. Average pore water velocity in the improved column design is about the same as in the old design, that is, about 1×10^{-5} cm/sec or less. By reducing the distance water has to travel, more pore volumes can be eluted in a given period of time for the same pore water velocities used in previous studies.

In order to provide the sample volume needed for chemical analysis at fractional pore volumes, the flow-through area was increased. The diameter selected for the improved column design is 25 cm. This diameter provides sufficient sample volume for chemical analysis of fractional pore volumes (Myers, Gambrell, and Tittlebaum 1991). As a consequence of reducing length and increasing diameter, the improved column leaching apparatus is a thin-layer column resembling a pancake. Side-wall effects were also considered in selecting the diameter for the improved column design (Myers, Gambrell, and Tittlebaum 1991). Review of work by Montgomery (1978) on column settling tests for dredged material and the theoretical work of Sommerton and Wood (1988) showed that side-wall effects should be minimal for the improved column design.

The new column design also incorporates improvements in flow delivery and control. Up-flow mode of operation using a constant-volume pump provides better flow control than was possible using down-flow and pressure in the old design. In the old design, flow was controlled by manual adjustment of operating pressure. Because pressure adjustment could not be made continuously, flow typically fluctuated from the average flow calculated for an entire study period. Flow provided by a constant-volume pump eliminates or significantly reduces variations in flow. This is an important advantage because the model equation (Equation 2) assumes flow is constant. Thus, the improved column design should more closely approximate model assumptions than the old design.

The distribution disks and the concentric and radial groves in the improved column design also improve experimental approximation of model assumptions. Equation 2 is a one-dimensional equation; that is, flow is in only one direction. With the old design, no collection gallery for the leachate exit was provided. Throughout most of the sediment profile, flow was probably one-dimensional, but near the column exit, two-dimensional flow in the sediment was necessary. In the improved column design, two-dimensional flow will be restricted to grooves in the end-plates, and flow is one-dimensional throughout the sediment profile.

5 Interpretation of Results

Information Provided by SBLTs

SBLTs provide two types of information that can be used when evaluating potential leachate impacts: maximum potential leachate concentration of contaminants, and extrapolations of these predictions to comparable sediment having different concentrations of the same contaminant. The test provides a series of leachate concentrations, one concentration per leach cycle for a particular contaminant. The two most commonly observed trends in freshwater leachate concentrations are decreasing contaminant concentrations with increasing leach cycle number and contaminant concentrations that show little or no change. Without further manipulation, the concentration data provide an estimate of maximum leachate concentration for a particular contaminant. The leach cycle concentrations can also provide information on contaminant partitioning between sediment and water. Following the procedures described in Chapter 3 of this report, contaminant distribution coefficients K_ds can be obtained if the leachate concentrations decrease with increasing leach cycle number. These distribution coefficients can be used to characterize the source term in Equations 1 and 2. The K_d can also be used for predicting leachate concentrations from sediment of the same type with different contaminant concentrations within different areas of a CDF.

Contaminant Concentration and Mass Flow

Leachate generation and transport depend on site-specific hydrology, engineering controls at the disposal site, dredged material hydraulic conductivity, initial water content, and nature of contaminants. Therefore, evaluation of potential leachate impacts will be greatly affected by the nature of the site and the engineering controls in place. Varying the engineering controls during the evaluation also allows selection of the optimum controls.

Two aspects of leachate generation from CDFs are of particular concern, leachate contaminant concentrations and leachate flow. Comparisons between drinking water and surface water standards and maximum leachate concentrations can be used to provide an early indication of potential leachate problems. If appropriate standards are not exceeded, such comparisons may be all that is needed for leachate evaluation. Surface water standards should be used only if the leachate is leaving the site and impacting surface waters. The biggest change brought about by CDF control measures is in the amount of leachate mass flow. For example, flow through a 1-m lift of the same dredged material will be higher from a 2-ha site than from a 1-ha site with the same rainfall and climate. Comparisons between drinking water or surface water standards and leachate concentrations cannot be used to make management decisions on CDF leachate control measures. Leachate concentrations at the site boundaries (interface between dredged material and the CDF lining) will generally be similar regardless of the control measures used.

Leachate flow in conjunction with leachate contaminant concentration determines the mass of contaminant that can potentially leave the site boundaries. Contaminant mass leaving site boundaries is particularly important when comparing the effects of various CDF disposal options such as depth of fill, drainage of surface water, and other leachate control measures such as collection and treatment.

To determine leachate mass flow, site-specific considerations of factors affecting leachate generation must be considered. After dredging and disposal, dredged material is initially saturated (all voids are filled with water). As evaporation and seepage remove water from the voids, the amount of water stored and available for gravity drainage decreases. After some time, usually several years for conventional CDF designs, a quasi-equilibrium is reached in which water that seeps or evaporates is replenished by infiltration through the surface. The amount of water stored when a quasi-equilibrium is reached and the amount released before a quasi-equilibrium is reached depend primarily on local hydrology, dredged material properties, and facility design factors. To predict time-varying leachate flow, all of these factors must be considered.

Preproject estimation of leachate flow, therefore, requires coupled simulation of local weather patterns and hydrologic processes governing leachate generation. Important climatic processes and factors include precipitation, temperature, and humidity. Important hydrologic processes include infiltration, snowmelt, runoff, and evaporation. Important subsurface processes include evaporation from dredged material voids and flow in unsaturated and saturated zones. The Hydrologic Evaluation of Landfill Performance (HELP) model (Schroeder et al. 1988) can be used to simulate these processes for selected disposal scenarios.

HELP is a hydrologic water budget model that accounts for the effects of surface storage, runoff, infiltration, percolation, evapotranspiration, soil moisture storage, lateral drainage to leachate collection systems, and

percolation through liners. Alternative scenarios can be selected and evaluated using the HELP model to estimate percolation rates and to compare control measures. Scenarios that have been evaluated include (a) land farming with different lift depths, (b) different lift depths inside CDFs with no engineering controls other than routine operation and management for drainage of surface runoff, and (c) extensive CDF management with leachate collection system and a composite liner (Lee et al. 1992; Brannon, Myers, and Price 1992).

For CDF sites where groundwater flows directly into the material, more complex modeling operations may be needed to predict the movement and concentration of contaminants at the CDF boundaries. Flow of anaerobic leachate through oxic dikes is another complicated situation potentially requiring complex modeling to predict contaminant concentrations.

Comparison of Batch and Column Results

Prediction of long-term contaminant leaching requires proper mathematical formulation of the source term in Equations 1 and 2. The applicability of source terms based on sequential batch leach data is determined with an integrated approach (Figure 11). Parameters from SBLTs, soil
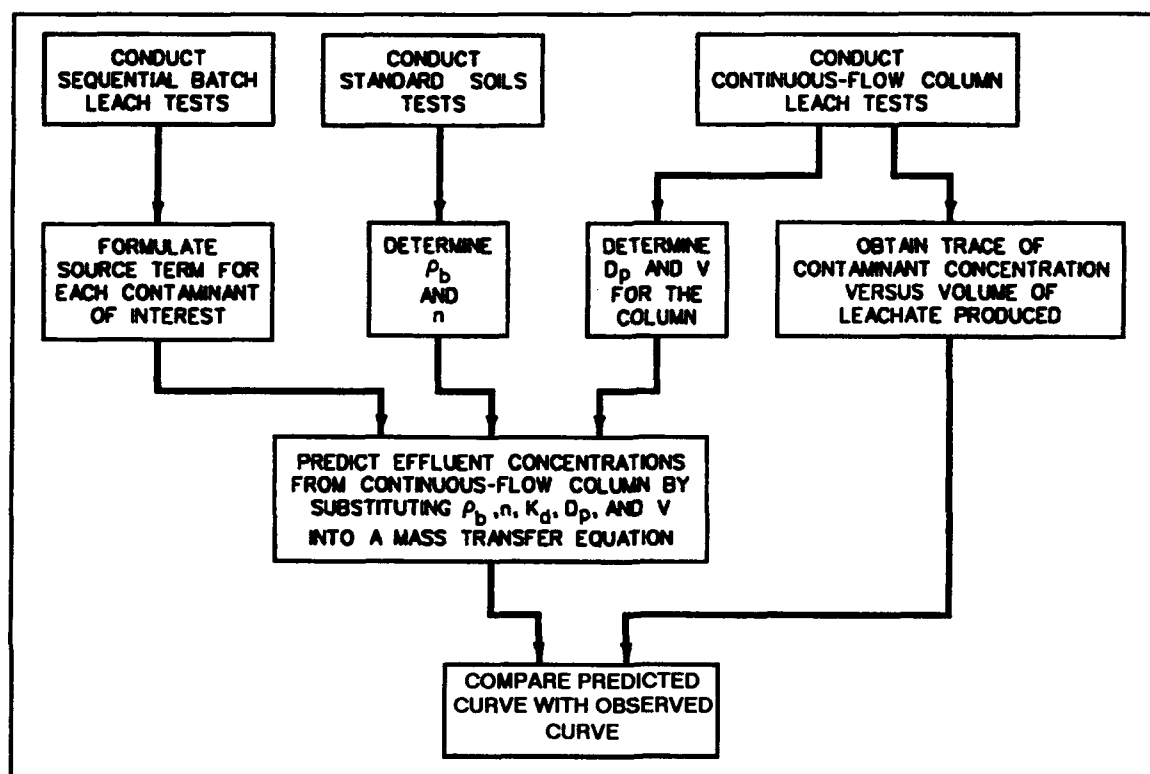

Figure 11. Integrated approach for examining the source term

tests, and column operating records are used in a contaminant transport equation to predict column elution concentrations. Predictions can then be compared with observed elution behavior. If predicted and observed column elution data agree, the processes governing transfer of contaminants from dredged material solids to water have been adequately described. If not, other source term formulations may be needed. Once interphase transfer has been adequately described, contaminant migration by leaching can be evaluated for the flow conditions that apply in the field.

Details of the mathematics involved in comparing batch and column leaching results as well as results of such comparisons are presented in Brannon, Myers, and Price (1992).

6 Conclusions

An SBLT has been developed to provide a short-term laboratory test that describes the distribution of contaminants between aqueous and solid phases as sediment solids are exposed to increasing amounts of water. Column leach tests have been developed as laboratory-scale physical models of contaminant leaching in a CDF.

Sequential batch leach tests are recommended for leachate evaluations of freshwater sediments. Column leach tests, while not recommended for routine use, may be conducted when the contamination potential of the dredged material is high and independent confirmation of batch test results is desired.

The SBLT provides information on the maximum potential leachate concentration of contaminants and can provide predictions of leachate quality for comparable sediment having different concentrations of the same contaminant. Use of leachate test results in conjunction with the HELP model is recommended for preproject evaluation of leachate control options. When it is necessary to also conduct column leach tests, an integrated approach for coupling SBLT information with mass transport equations is provided in order to compare the results of batch and column tests.

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Appendix A
Anaerobic Sequential Batch
Leach Testing

Scope

This appendix provides the user with detailed guidance on the conduct of the anaerobic sequential batch leach testing.

Summary of Procedure

Sediment is prepared and loaded into centrifuge tubes under anaerobic conditions at a 4:1 water-to-sediment ratio, then sequentially leached for 24 hr with distilled-deionized (DDI) water. Leachate is separated from sediment by centrifugation, and the leachate is chemically analyzed. Fresh DDI water is added to the centrifuge tube to replace that removed, and the process is repeated a minimum of four complete cycles.

Materials and Apparatus

Materials and aparatus are listed below:

a. 450-mL stainless steel centrifuge tubes for organic contaminants.

b. 250-mL polycarbonate centrifuge tubes with leakproof caps for metals.

c. Weighing scale with sufficient capacity to accurately weigh centrifuge bottle, cap, and added sediment and water.

d. Glove box of sufficient size to contain centrifuge bottles, sediment, and scale.

e. High purity nitrogen gas.

f. Vacuum source.

g. Mechanical mixer.

h. Stainless steel spatula.

i. Paper towels.

j. Glass fiber filter, 1 μm, 47 mm diameter, binder free (Gelman Type A/E or equivalent).

k. Glass fiber prefilters, 4 μm, 47 mm diameter, binder free (Whatman Type GD/F or equivalent).

l. Cellulose acetate filters, 0.45 μm, 47 mm diameter (Millipore or equivalent).

m. Filtration manifolds for organics and metals.

n. High capacity tumbler.

o. Muffle furnace.

p. Oxygen meter.

q. 1-L amber glass sample bottles for organic contaminants.

r. 250-mL plastic sample bottles for metals.

s. Contaminated sediment.

Reagents

Reagents include:

a. DDI water conforming to ASTM Type II (ASTM D1193-77).

b. Concentrated HCl.

c. Concentrated Ultrex HNO_3.

Procedure

The procedure includes the following steps:

a. For organic contaminant leaching, use clean stainless steel centrifuge tubes, stainless steel spatulas, and glass filtration apparatus according to instructions for analysis of organic contaminants in SW-846, "Test Methods for Evaluating Solid Waste," USEPA, Office of Solid Waste and Emergency Response, Washington, DC 20460. Combust glass fiber filter and prefilter at 400 $^\circ$C for 15 min.

b. For metal contaminant leaching, use clean polycarbonate centrifuge tubes, stainless steel spatulas, and polycarbonate filtration apparatus according to instructions for metals analysis in SW-846.

c. Prepare forms and labels. Conduct percent solids determination on mixed sediment sample and calculate solids and water content and required weights of water and sediment to achieve a water-to-solids ratio of 4:1 (weight of pore water + weight of DDI water/dry weight of sediment).

d. Seal the glove box, and using alternate vacumn and nitrogen addition, purge and vent until the oxygen meter registers 0 percent. Ensure that a slight overpressure of nitrogen exists inside the glove box. This can be determined by observation of a slight expansion of the rubber gloves attached to the glove box.

e. Add all necessary equipment to the glove box through the airlock. Cycle as necessary to remove any residual oxygen.

f. In the glove box, remix the sediment to ensure uniformity. Place a centrifuge bottle with cap on the balance and re :ord the weight. Tare the centrifuge bottle and cap and load with sediment to the desired weight. Record the weight of the sediment added. Tare the centrifuge bottle, cap, and added sediment and add DDI water to bring the final water-to-sediment ratio to 4:1. Wipe sediment from any surface that contacts the O-ring of the leakproof top. Record the weight of DDI water, then zero the balance and record the weight of bottle, cap, sediment, and leach water. Bottles should be loaded such that pairs of bottles balance to within 2 g. For organic contaminants, multiple bottles may be required to obtain sufficient leachate (1 L) for chemical analysis.

g. Ensure that all centrifuge bottles are sealed, then remove the bottles from the glove box and transfer them to a tumbler. Tumble the samples for 24 hr at a rate of 40 rpm. Record the time tumbling starts and stops.

h. Remove the centrifuge bottles from the tumbler and place paired bottles opposite one another in a refrigerated centrifuge. Centrifuge stainless steel tubes for organic contaminant analysis at 6,500 × g for 30 min. Note: Stainless steel centrifuge tubes are heavy, limiting the speed of centrifugation. Leachates for metals are centrifuged at 9,000 × g.

i. Assemble the decontaminated filtration apparatus. For organic contaminants, the 4-μm prefilter is placed over the 1-μm glass fiber filter. Filter the samples, maintaining a nitrogen atmosphere over the samples while filtration is ongoing. Acidify leachate for organic analysis with 1 mL of concentrated HCl per liter of leachate to prevent iron precipitation and organic scavenging, then transfer sample to a precleaned, 1-L amber glass bottle. Bottles for analysis of organic contaminants should be filled to the top. For metals, much the same procedure is followed. Filter the sample through a 0.45-μm filter and acidify with 1 mL of concentrated Ultrex nitric acid per liter of leachate. Transfer leachate samples to plastic bottles for storage and analysis.

j. In the deoxygenated glove box, record the weight of the centrifuge bottle with lid and sediment after filtering. Repeat with remaining samples.

k. Add DDI water to the centrifuge tubes to bring them back to the same water-to-solids ratio of 4:1. Record the weight of bottle with lid, DDI water, and sediment. Repeat with remaining samples.

l. Tumble samples and centrifuge as described in steps *g-i*. Repeat a minimum of four times.

m. Using DDI water, prepare and run a procedure blank according to the procedure described above for one cycle.

n. Using DDI water prepare a lab blank.

Appendix B
Thin-Layer Column Leach
Apparatus Assembly and Loading

Scope

This standard operating procedure instructs the user on procedures for assembling, loading, and maintaining column leach apparatus.

Summary of Procedure

Contaminated sediment is mixed, weighed, and loaded into the column leach apparatus. Deoxygenated, distilled-deionized (DDI) water is introduced into the loaded column over an extended time interval. Water flow is controlled by a constant-volume flow pump. Leachate samples are collected at specified time intervals and are analyzed for specific parameters.

Materials and Apparatus

Materials and apparatus are listed below:

a. Column leach apparatus (Figure B1).

b. Kilogram weighing scale.

c. Two 9/16-in. open-ended wrenches.

d. One 10-in. crescent wrench.
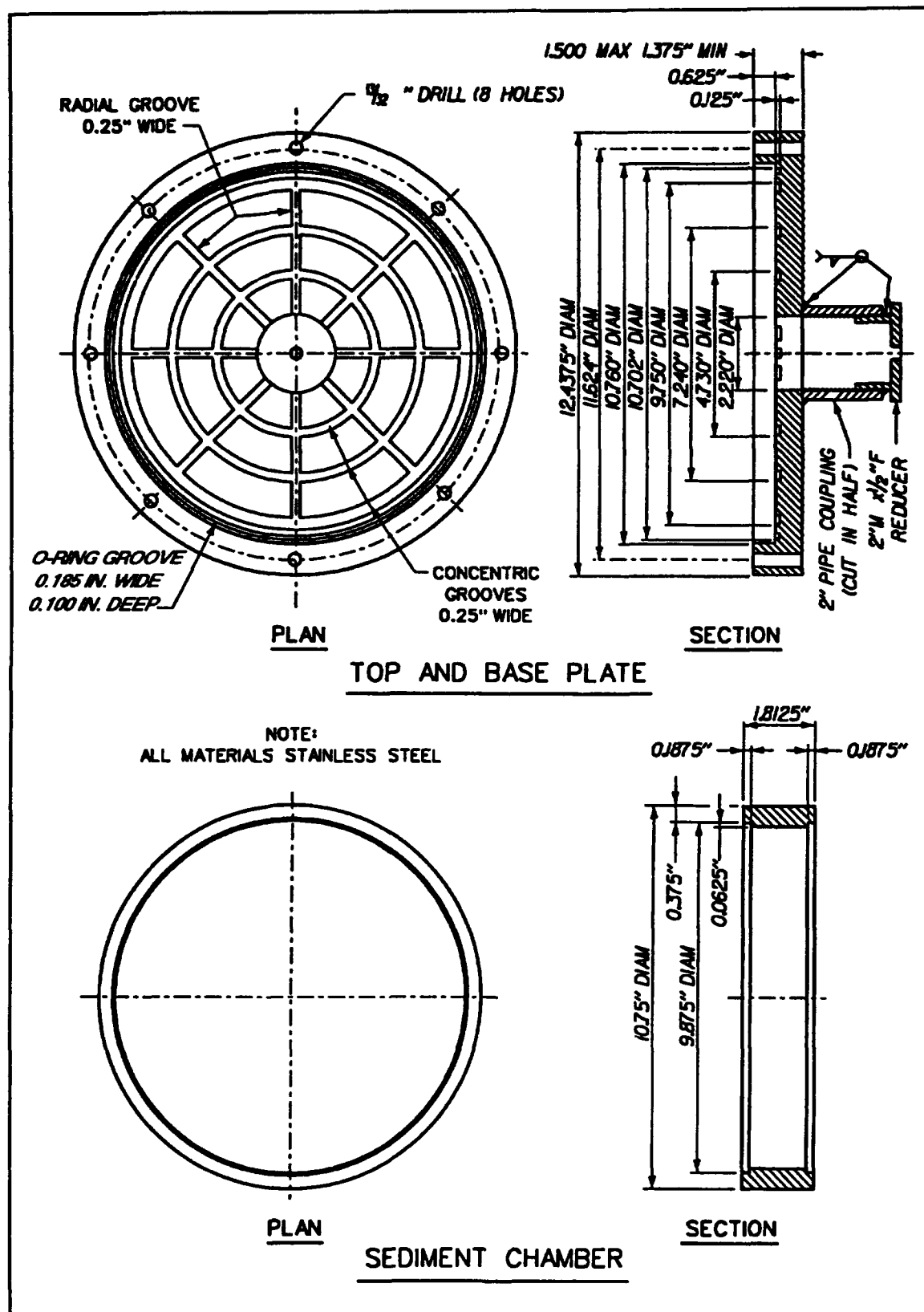
e. Mechanical mixer.

f. Polyethylene beaker (5,000 mL).

Figure B1. Shop drawing of thin-layer column

g. Stainless steel spatula, 12 in.

h. Stainless steel spatula, 6 in.

i. Polyethylene scoop.

j. Paper towels.

k. Glass fiber filter, 1 μm, 257 mm diameter, binder free (Gelman Type A/E or equivalent).

l. Polyethylene gloves.

m. Teflon tubing (ID 5/32 in., OD 1/4 in.).

n. Contaminated sediments.

o. Constant-volume metering pump (Example: Fluid Metering, Inc., model QG6-0-SSY and QG6-2-SSY).

p. Dial indicator kit (Example: Fluid Metering, Inc., model Q485-1).

q. O-rings (ring diameter 10.75 in., OD 0.157 in.).

r. Stainless steel plug valve (Example: Hoke model 7312G4Y).

s. Stainless steel tubing (OD 1/4 in., ID 1/8 in.).

t. Stainless steel tubing (OD 1/8 in.).

u. Compression fittings (1/4 in. $\times$ 1/2 in.) and (1/4 in. $\times$ 1/8 in.).

v. 5-gal glass bottle.

w. Support table for columns.

x. Detergent

Reagents

Reagents include DDI water conforming to ASTM Type II (ASTM D1193-77).

Procedure

The steps to follow are listed below:

a. Assemble the fluid metering pump and dial indicator kit according to manufacturers' instructions.

b. Clean the column parts with a liquid, nonionic, metal-free detergent solution; rinse thoroughly with DDI water; and let dry.

c. Screw the nuts onto the bottom of the threaded rods and insert the rods through the column base plate. Place the base plate in the 3-in.-diam hole on the table.

d. Using 1/4 in. × 1/2 in. compression fittings, attach a 2-in. piece of 1/4-in. stainless steel tubing to the inlet of the base plate. (Note: Use 1/4 in. × 1/2 in. compression fittings to make all stainless steel/Teflon tubing/plug valve/fluid pump connections.)

e. Connect a stainless steel plug valve to the 2-in. piece of stainless steel tubing. Use a suitable length of 1/4 in. OD Teflon tubing to connect the plug valve to the outlet side of the fluid metering pump.

f. Attach a suitable length of 1/4-in. OD Teflon tubing to the inlet side of the pump, and insert the opposite end of this tubing in a 5-gal glass bottle filled with deaired, DDI water. Securely cover the mouth of the bottle with parafilm.

g. Open the plug valve, and turn on the fluid pump. When the water level reaches the grooves inside the base plate, turn off the pump.

h. Place an O-ring inside the base plate making sure the O-ring is properly seated to avoid water leakage. Place a distribution disk in the base plate. Place a glass fiber filter on top of the distribution disk. Place the sediment chamber in the base plate, properly aligning it on top of the O-ring.

i. On a mechanical mixer, carefully mix the sediment. Mixing under an oxygen-free atmosphere is recommended.

j. Weigh the 5,000-mL beaker, spatula, and scoop. Use the scoop to transfer approximately 4 kg of sediment to the beaker. Record the total weight of the sediment, beaker, spatula, and scoop.

k. Slowly fill the sediment chamber with sediment from the beaker, while carefully avoiding entrapment of air bubbles. When the sediment is level with the top part of the sediment chamber, carefully smooth the surface of the sediment with the spatula. (Note: In

order to properly seat the top distribution plate, clean the groove in the sediment chamber.)

l. Place a distribution plate on top of the sediment chamber. Place a glass fiber filter on top of the distribution plate. Wet the O-ring before placing it in the top groove of the sediment chamber.

m. Carefully place the top plate on the sediment chamber, aligning the plate with the threaded rods in the base plate. Tighten all nuts. Connect 1/4-in. stainless steel tubing to the outlet of the top plate.

n. Connect a suitable length of stainless steel or Teflon tubing to the outlet of the top plate. (Teflon is recommended for leaching of metals.)

o. Set the dial indicator to obtain the correct flow rate for experimental conditions. Turn on the fluid pump, carefully check all areas for leaks, and tighten connections if necessary.

p. Reweigh the beaker, spatula, scoop, and sediment remaining in the beaker. Determine the weight of sediment in the column leach apparatus, by difference, and record this weight.

Appendix C
Collection and Preservation of Column Leachate Samples for Total Metal, Chloride Ion, Total Organic Carbon, pH, and Electrical Conductivity Analyses

Scope

This procedure describes the collection and preservation of samples generated from leaching of sediment and dredged material in laboratory column leaching apparatus.

Summary of Procedure

Column leachate samples are collected at a prescribed frequency, preserved with acid to pH < 2, and stored at 4 °C prior to metals, chloride ion, and total organic carbon (TOC) analyses. The pH and electrical conductivity are determined on discrete nonacidified samples.

Materials

Materials used include:

a. Analytical balance.

b. pH paper.

c. Parafilm, minimum 4 in. in width.

d. Labeling tape.

e. pH meter.

f. Electrical conductivity meter.

g. Clamp, large.

h. Ring stand.

i. Pipetter.

j. Pipet tips: 1 mL, 5 mL.

k. Polyethylene stirring rods.

l. Polyethylene bottles: 60, 250, 500, 1,000 mL.

Note: All plasticware must be prewashed with a metal-free, nonionic detergent solution, rinsed, soaked in 1 + 1 nitric acid for 24 hr, and rerinsed in distilled-deionized (DDI) water.

Reagents

Reagents include:

a. DDI water conforming to ASTM Type II water (ASTM D1193-77).

b. Ultrex nitric acid, concentrated (J.T. Baker).

c. Ultrex sulfuric acid, concentrated (J.T. Baker).

Procedure

The procedure includes:

a. Sample preservation

(1) Place two strips of labeling tape on each polyethylene sample collection bottle. Consult the sample collection chart in Table C1, and then pipette 0.5 mL DDI water and 0.5 mL concentrated Ultrex nitric acid per 100 mL of leachate sample for metal analysis into the polyethylene bottle. For TOC analysis, pipette 0.5 mL DDI water and 0.5 mL of concentrated Ultrex

sulfuric acid into the collection bottle. Weigh the bottle and lid, and record this weight on one strip of labeling tape.

(2) On the other strip of tape, label each collection vessel with the sediment identification, column leach apparatus number, sample number, and parameter code. Suggested parameter codes are M = metals, C = chloride, T = total organic carbon, and PE = pH and electrical conductivity.

(3) Remove the lid, and securely cover each bottle with parafilm. Puncture a small hole in the center of the parafilm with a pipette tip.

(4) Attach a large clamp to a ring stand, and secure the collection bottle to the clamp. Place the bottle under the column leach apparatus, tilting and elevating the bottle in such a manner that the end of the outlet tubing is in contact with the acid solution in the bottle. Tightly seal the parafilm around the outlet tubing.

b. Sample collection.

(1) Collect leachate samples at a prescribed frequency. Recommended frequency is provided in the sample collection chart listed in Table C1.

(2) After collection, replace the lid, carefully mix the leachate sample, and reweigh. Determine the weight of sample collected, by difference, and record this weight.

(3) Insert a polyethylene stirring rod in the sample, and check the pH of the sample with pH paper. If the pH of the sample is greater than 2, add concentrated Ultrex nitric acid in 0.1-mL increments until the pH is less than 2.

(4) For chloride determination, weigh 40 g of leachate sample into a 60-mL polyethylene bottle. Label the bottle with the sediment identification, column leach apparatus number, sample number, and parameter code. Store samples at 4 °C.

(5) After each metal/chloride and TOC leachate sample has been collected, place a labeled, preweighed 20-mL polyethylene bottle under the column outlet. Collect approximately 12 g of leachate. (Reweigh the bottle to determine the exact weight of leachate.) Check the pH and electrical conductivity of this sample on a pH meter and electrical conductivity meter.

Table C1
Sample Collection Chart

Sample Number	Approximate Sample Size, g	
	Metals	TOC
1	250	100
2	250	100
3	250	100
4	250	100
5	250	100
6	250	100
7	500	250
8	500	250
9	500	250
10	500	250
11	500	250
12	500	250
13	500	250
14	500	250
15	500	250
16	500	250
17	500	250
18	500	250
19	500	250
20	1000	500
21	1000	500
22	1000	500
23	1000	500
24	1000	500
25	1000	500
26	1000	1000
27	1000	1000
28	1000	1000
29	1000	1000
30	1000	1000

Appendix D
Collection and Preservation of Column Leachate Samples for Analysis of Organic Constituents

Scope

This procedure describes collection and preservation techniques for samples generated from leaching of sediments and dredged materials in laboratory column leaching apparatus.

Summary of Procedure

Column leachate samples are collected in amber glass bottles in a prescribed manner. The samples are stored at 4 °C, then analyzed for polycyclic aromatics hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and other related organic constituents.

Materials

Materials used include:

a. Analytical balance.

b. Labeling tape.

c. Fraction collector, with the capability of time-based sample collection in seconds or minutes (Example: Eldex Laboratories, Inc., model UP-1A).

d. Silicone tubing, plasticizer-free, additive-free (1/8 in. ID × 1/4 in. OD and 1/4 in. ID × 3/8 in. OD).

e. Amber glass bottles with Teflon-lined lids, precleaned to EPA Level 1: 1,000 mL.

Reagents

Reagents utilized are:

a. DDI water conforming to ASTM Type II (ASTM D1193-77).

b. Methanol, pesticide grade or equivalent.

Procedure

This procedure requires:

a. Preparation of fraction collector.

(1) Assemble the fraction collector according to manufacturer's instructions and place it on the table near the column leach apparatus described in Appendix B. Attach a 12-in. section of silicone tubing (1/8 in. ID × 1/4 in. OD, cleaned with methanol and rinsed repeatedly with DDI water) to the outlet tubing on the column leach apparatus.

(2) Attach 1/8-in. ID silicone tubing to the bottom of the glass tubes on the fraction collector. (This silicone tubing will be later connected to 1/8-in. stainless steel tubing inserted in lids used to cover the amber bottles during sample collection.)

(3) Remove the lids from two 1-L amber bottles. Drill four 1/8-in.-diam holes in each lid. Insert pieces of 1/8-in. stainless steel tubing, equal to the height of the amber glass bottle (plus about 2 in.), through each hole.

b. Sample collection.

(1) Place a strip of labeling tape on each amber sample collection bottle. Weigh the bottle and lid, and record this weight on the tape.

(2) Label each collection vessel with the sediment identification, column leach apparatus number, sample number, and parameter

code. Suggested parameter codes are PAH = polycyclic aromatic hydrocarbons, PCB = polychlorinated biphenyls.

(3) Remove the lids from the weighed bottle and replace them with the lids described in Step *a*(3). Place the bottle on the base of the fraction collector. Connect the silicone tubing described in Step *a*(2) to the stainless steel tubing on top of the lids.

(4) Set the time-based control module on the fraction collector to collect a minimum of 500 mL of leachate sample per collection vessel.

c. Sample preservation.

(1) After collection, place the original lid on each leachate sample and reweigh. Determine the weight of sample collected, by difference, and record this weight.

(2) Immediately after collection, store samples at 4 °C.

Appendix E
Digestion of Samples for Total Metal Analysis

Scope

This digestion procedure is used to prepare aqueous leachate samples that may contain insoluble colloidal particulates for analysis by flame atomic absorption spectroscopy (FLAA) or inductively coupled plasma spectroscopy (ICP). The procedure is used to determine total metal content. (Reference SW846 Method 3010.)

Summary of Test Method

Nitric acid is added to a specified volume of the sample. The sample is refluxed with additional portions of nitric acid until the digestate is clear or the color is stable. The sample is then refluxed with hydrochloric acid and brought up to volume. The digested sample is analyzed for cadmium, chromium, copper, iron, lead, manganese, nickel, and zinc.

Materials and Apparatus

Materials and apparatus include:

a. Fume hood.

b. Hot plate.

c. Safety glasses and polyethylene gloves.

d. Volumetric flasks, 100 mL.

e. Qualitative filter paper (Whatman # 40 or equivalent).

f. Polyethylene bottles, 125 mL.

g. Glass stirring rods.

h. Glass filtering funnel.

i. Teflon beaker covers.

j. 250-mL Teflon beakers.

k. Pipetter.

l. Pipet tips.

Note: All glassware and plasticware must be prewashed, rinsed, soaked in 1:1 nitric acid, and rerinsed in distilled-deionized (DDI) water.

Reagents

Reagents include:

a. Ultrex nitric acid, concentrated (J.T. Baker).

b. Ultrex hydrochloric acid, concentrated (J.T. Baker).

c. DDI water conforming to ASTM Type II Water (ASTM D1193-77).

d. 1:1 nitric acid.

Digestion Procedure

The digestion procedure is as follows:

a. Mix the aqueous leachate sample thoroughly. Pour a 100-mL aliquot into a 100-mL volumetric flask. Transfer the sample to a 250-mL Teflon beaker. Add 3 mL concentrated Ultrex nitric acid, and partially cover the beaker with a Teflon beaker cover.

b. Place the beaker on a hot plate set at 95 °C. Cautiously evaporate the contents to <10 mL, making certain that the sample does not boil and that no portion of the bottom of the beaker is allowed to evaporate to dryness.

c. Cool the beaker and add another 3-mL portion of nitric acid. Completely cover the beaker, return it to the hot plate, and allow the sample to reflux, gently.

d. Continue heating and adding additional acid in 3-mL increments until the digestion is complete, as evidenced by a light color or an unchanging color.

e. Cool the beaker and add 10 mL of 1:1 hydrochloric acid. Cover the beaker, and reflux for an additional 15 min to dissolve any precipitate or residue resulting from evaporation. Wash down the cover and walls of the beaker with small portions of DDI water.

f. Place a piece of filter paper in a filtering funnel. Prerinse the filter paper with 1:1 Ultrex nitric acid and discard this rinsate.

g. Place a 100-mL volumetric flask under the filtering funnel. To remove silicates and other insoluble matter, filter the hot digested sample into the volumetric flask. Rinse the beaker with small portions of DDI water and pour this rinsate through the filter paper.

h. Let the sample cool to room temperature, then dilute to 100 mL volume with DDI water. Mix, then pour the sample into a prelabeled 125-mL polyethylene bottle.

Quality Control

Quality control measures include:

a. For each analytical batch of samples processed, carry a blank, consisting of 100 mL of DDI water, through the entire digestion procedure.

b. With each set of samples, process a duplicate and spiked sample, and a standard reference material.

Appendix F
Chloride Ion Determination by Ion-Selective Electrode

Scope

This test method covers the determination of chloride ion in aqueous leachate samples. Samples containing 2 to 1,000 mg/L chloride ion may be analyzed by this procedure. Samples containing higher concentrations of chloride ion may be analyzed after dilution of an appropriate aliquot of the sample.

Summary of Test Method

Chloride ion is measured potentiometrically using a chloride ion selective electrode in conjunction with a double junction, sleeve-type reference electrode. An equal volume of chloride ionic strength adjuster (CISA) is added to an equal volume of standard and sample. Potentials are measured on an ion-selective meter. (Reference ASTM Method D 512-89.)

Interferences

The CISA minimizes interferences from up to 500 mg/L sulfide, 1,000 mg/L bromide or iodide, a hundredfold excess of cyanide over chloride, and 1,000 mg/L ammonia.

Materials and Apparatus

Materials and apparatus include:

a. Ion-selective meter (Example: Orion model 720A).

b. Chloride-ion selective electrode (Orion model 9417B or equivalent).

c. Double-junction reference electrode (Orion model 90-02 or equivalent).

d. Chloride-ion filling solutions (outer chamber, Orion model 900003 or equivalent; inner chamber, Orion model 900002 or equivalent).

e. Magnetic stirrer.

f. Teflon-coated magnetic stir bars.

g. Magnetic stir bar retriever.

h. Analytical balance.

i. Oven.

j. Protective gloves.

k. 1,000-mL volumetric flasks.

l. 1,000-mL polyethylene jars.

m. 30-mL glass beakers.

n. 1-, 2-, 10-, 25-, 50-, and 100-mL volumetric pipets.

o. 1,000-mL glass beaker.

p. Fume hood.

Reagents

Reagents include:

a. Distilled-deionized (DDI) water conforming to ASTM Type II water (ASTM D1193-77, 1983).

b. Instrument performance check (IPC) (3,000 mg/L chloride). In a 1-L volumetric flask, dissolve 6.31 g reagent-grade potassium chloride (dried for 1 hr at 500 °C) and dilute to volume with DDI water.

c. Quality control (QC) sample (300 mg/L chloride). Pipet 100 mL of the 3,000 mg/L chloride into a 1-L volumetric flask and dilute to volume with DDI water.

d. CISA. Weigh 15.1 g of reagent-grade sodium bromate (dried for 1 hr at 100 °C) and dissolve in 800 mL water. Pipet 75 mL of concentrated nitric acid. Stir well. Transfer to a 1-L volumetric flask and dilute to volume with DDI water. Store CISA in a polyethylene bottle. (CAUTION: Sodium bromate is a strong oxidant and should be handled appropriately. Preparation and dilutions of CISA should be made in a fume hood.)

e. Chloride stock solution (1,000 mg/L chloride). In a 1-L volumetric flask, dissolve 1.648 g of reagent-grade sodium chloride (dried for 1 hr at 600 °C) in DDI water and dilute to volume.

f. Chloride standard solutions (1, 2, 10, 50, 100, and 500 mg/L chloride). Using volumetric pipets, transfer 1, 2, 10, 50, 100, and 500 mL of the 1,000-mg/L chloride stock solution into separate 1-L volumetric flasks. Dilute each to 1 L with DDI water.

Calibration Curve Preparation

Calibration curve preparation is as follows:

a. Following the manufacturer's instructions, fill the inner and outer chamber of the double-junction reference electrode. Connect the electrodes to the ion-selective meter.

b. Pipet 10 mL of the 2-, 10-, 50-, 100-, 500-, and 1000-mg/L chloride solutions in separate 30-mL beakers containing magnetic stirring bars. Add 10 mL of the CISA reagent. Stir each for 2 min magnetically.

c. Remove each beaker from the stirrer, retrieve the magnetic stir bars, and wait 30 ± 2 min before inserting the electrodes in each standard. Wait for a stable reading, then record the potential of each standard, in millivolts. Between each measurement, thoroughly clean the electrodes with DDI water.

d. Prepare a spreadsheet consisting of the logarithm of the standards prepared in step *b* and corresponding millivolt values. Construct a standard calibration curve by plotting log concentration on the x-axis versus millivolt readings on the y-axis.

e. To determine the concentration of unknown samples, calculate the linear regression of concentration on the x-axis versus millivolt readings on the y-axis. Set up a formula that calculates x-intercept values from corresponding y-values:

$$y = mX + b$$

$$mX + b = y$$

Therefore,

$$X = (y - b)/m$$

where

  $y =$ known millivolt values

  $m =$ coefficient of X

  $X =$ unknown concentration

  $b =$ constant

Procedure for Measuring Samples

The procedure for measuring samples is listed below:

a. Place a magnetic stir bar in a 30-mL beaker with 10 mL of the sample and 10 mL of CISA reagent. Follow the instructions given in steps c and d under "Calibration Curve Preparation."

b. Calculate chloride concentration of the sample, in milligrams per liter, according to step e above.

  (1) If the chloride concentration is greater than 1,000 mg/L, dilute an appropriate aliquot of the sample into a 100-mL volumetric flask with DDI water.

  (2) Pipet 10 mL of the *diluted sample* into a 30-mL beaker containing 10 mL of CISA into the beaker. Measure the sample according to steps c and d above.

  (3) Calculate the concentration of the *diluted sample* as follows:

  $$C = A \times B$$

  where

  $C =$ concentration, mg/L

  $A =$ calculated concentration value, mg/L (step e above)

  $B =$ dilution ratio.

Quality Control

Quality control measures include:

a. Instrument performance check: Each time the ion-selective meter is operated, monitor performance by measuring the potential of the IPC. Do *not* add CISA to the IPC sample.

b. Quality control sample: Prior to analyzing samples, analyze the 300-mg/L chloride quality control sample in the same manner as samples are analyzed.

c. Duplicates and spikes: After every 10th sample, analyze a duplicate and a spiked sample.

d. Standard reference material: Analyze a standard reference material with each batch of samples analyzed.

e. Contamination evaluation: Following the instructions given in this section, evaluate contamination each time a group of samples is analyzed.

   (1) Into a 30-mL beaker, pipet 10 mL DDI water and 10 mL CISA reagent. (Note: This solution is the reagent blank used for contamination evaluation of the reagents).

   (2) Into another 30-mL beaker, pipet 10 mL of 1-mg/L chloride standard solution and 10 mL CISA reagent. Place a stir bar in each solution. Place each solution on the magnetic stirrer, stir for 2 min, remove the beakers from stirrer, and wait 30 ± 2 min.

   (3) Place the electrodes in the water/CISA solution. Record the millivolt reading. (This solution contains no added chloride, and the potential reading will not be very stable.)

   (4) Rinse the electrodes thoroughly and place them in the 1-mg chloride/CISA mixture. Wait 1 to 2 min, measure, and record the results in millivolts.

       (NOTE: If the difference in readings between the water/CISA solution and the 1-mg/L chloride solution is less than 10 mV, the reagents are contaminated with chloride that will affect low-level concentrations. Uncontaminated reagents must be obtained.)

Appendix G
Bromide Ion Determination by Ion Selective Electrode

Scope

This test method covers the determination of bromide ion in aqueous leachate samples. Samples containing 1 to 1,000 mg/L bromide may be analyzed by this procedure. Samples containing higher concentrations of bromide ion may be measured after dilution of an appropriate aliquot of the sample.

Summary of Test Method

Bromide ion is measured potentiometrically using a bromide ion selective electrode in conjunction with a single-junction, sleeve-type reference electrode. The electrodes are calibrated in bromide solutions of known concentrations. An ionic strength adjuster (ISA) is added to both standards and samples. Potentials, in millivolts, are measured on an ion-selective meter.

Interferences

ASTM D 1246-88 lists interferences.

Materials and Apparatus

Materials and apparatus are listed below:

a. Ion-selective electrode meter (Example: Orion model 720A).

b. Bromide-ion selective electrode (Orion model 9435B or equivalent).

c. Single-junction, sleeve-type reference electrode (Orion model 90-01 or equivalent).

d. Single reference electrode filling solution (Orion model 900001 or equivalent).

e. Ionic strength adjuster (Orion model 940011 or equivalent).

f. Magnetic stirrer.

g. Teflon-coated magnetic stir bars.

h. Magnetic stir bar retriever.

i. Analytical balance.

j. Oven.

k. Polyethylene gloves.

l. 1,000-mL volumetric flasks.

m. 1,000-mL polyethylene jars.

n. 30-mL glass beakers.

o. 1/2-, 1-, 5-, 10-, 25-, 50-, and 100-mL volumetric pipets.

Reagents

Reagents include:

a. Distilled-deionized (DDI) water conforming to ASTM Type II water (ASTM D1193-77).

b. Instrument performance check (IPC) sample (4,000 mg/L bromide.). Dissolve 5.1514 g of potassium bromide (dried for 1 hr at 500 °C) in DDI water in a 1-L volumetric flask. Dilute to volume with DDI water.

c. Quality control (QC) sample (400 mg/L bromide). Pipet 100 mL of 4,000-mg/L bromide solution into a 1-L volumetric flask and dilute to volume with DDI water.

d. Bromide stock solution (1,000 mg/L bromide). In a 1-L volumetric flask dissolve 1.288 g of sodium bromide (dried for 1 hr at 500 °C) in DDI water and dilute to volume.

e. Bromide standard solutions (1, 5, 10, 50, and 100 mg/L bromide). Using volumetric pipets, transfer 1, 5, 10, 50, and 100 mL of the 1,000-mg/L bromide stock solution into separate 1-L volumetric flasks and dilute each to 1 L with DDI water.

Preparation of Calibration Curve

Calibration curve preparation is as follows:

a. Following the manufacturer's instructions, fill the outer chamber of the single-junction reference electrode with filling solution. Connect the electrodes to the ion selective meter.

b. Pipet 25 mL each of 1, 5, 10, 50, 100 and 1,000 mg/L of bromide standard solutions into separate 30-mL beakers containing magnetic stir bars. Add 0.5 mL ISA reagent and stir magnetically for 2 min.

c. Remove the beakers from the stirrer, retrieve the stirbars, and wait 15 ± 2 *min before inserting the electrodes in each standard.* When the reading stabilizes, record the potential of each standard in millivolts. Between each measurement, thoroughly clean the electrodes with DDI water.

d. Prepare a spreadsheet of the data from the logarithms of the standards prepared in step *b* and corresponding millivolt values. Calculate regression data. Construct a standard calibration curve by plotting log concentration on the x-axis versus millivolt readings on the y-axis.

e. To determine the concentration of unknown samples, use the regression data to set up a formula that calculates x-intercept values from corresponding y values:

$$y = mX + b$$

$$mX + b = y$$

Therefore,

$$X = (y - b)/m$$

where

$y =$ known millivolt values

m = coefficient of X

X = unknown concentration

b = constant

Procedure for Assaying Samples

The procedure for assaying samples includes:

a. Pipet 25 mL of leachate sample into a 30-mL beaker. Add 0.5 mL of the ISA reagent and stir on a magnetic stirrer for 2 min.

b. Remove the beaker from the stirrer, wait 15 ± 2 min and then insert the electrodes in the beaker. Wait 1 to 2 min for the reading to stabilize, then record.

c. To determine the bromide concentration in the sample, refer to step *e* under "Preparation of Calibration Curve."

   (1) If the bromide concentration is higher than 1,000 mg/L, dilute an appropriate aliquot of the sample into a 100-mL volumetric flask with DDI water.

   (2) Pipet 25 mL of the *diluted sample* into a 30-mL beaker. Add 0.5 mL of the ISA reagent. Measure the sample according to steps *b* and *c*.

   (3) Calculate the concentration of the *diluted* sample as follows:

   $C = A \times B$

   where

   C = concentration, mg/L

   A = calculated concentration value, mg/L

   B = dilution ratio

Quality Control

Quality control measures include:

a. Instrument performance check: Each time the ion-selective meter is operated, monitor instrument performance by measuring the potential, in millivolts, of the 4,000-mg/L bromide sample. Do not add ISA to the IPC sample.

b. Blank determination: Analyze a blank, daily.

c. Quality control sample: Prior to analyzing samples, analyze the 400-mg/L bromide quality control sample in the same manner as samples are analyzed.

d. Duplicates and spikes: Analyze a duplicate and spiked sample after every 10th sample.

e. *Standard reference material* (SRM): Analyze an SRM with each set of samples.

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